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(54) Photomagnetic disk with improved environmental resistance

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Details

1. Title of the invention

Photomagnetic disk with improved environmental resistance

2. Claim(s)

A photomagnetic disk having a photomagnetic recording medium layer and protective layer on the base sheet, wherein a resin comprising a polymeric portion mainly consisting of aromatic vinyl monomer and polyphenylene ether portion is used as a material for the base sheet.

3. Detailed description of the invention

Fields of industrial usage

This invention is regarding photomagnetic disk with lesser double refraction and excellent environmental resistance.

Conventional technique

Recently, various researches are carried out on the method of bit writing by laser for high-density recording method. Among these, photomagnetic disk consists of a photomagnetic recording medium layer and protective layer on the base sheet. The recording medium is heated locally by using laser light and data is written as 0, 1

information in the form of different direction of magnetization and, it is read by using magneto optical effect. This method differs from the punching method. As repeated writing and reading is possible, it is called as re - writable optical disk and a lot of development is going on.

The photomagnetic recording medium is obtained by forming vertical magnetic film (hereafter called as magnetic layer) comprising combination of rare earth metals (like Gd, Tb, Dy) and transition metals (like Fe, Co) by vapor deposition method or sputtering method on the base sheet. However, the magnetic layer alone has following defects.

- (1) Deterioration due to oxidation is fast and it cannot be used in practice.
- (2) It does not show sufficient photomagnetic effect and S/N ratio of reproduced signal is insufficient.

In order to solve above two problems, a sandwich structure usually having a magnetic layer of transparent dielectric material with appropriate refractive index, thickness (hereafter called as protective layer) is used. Various compounds such as oxides like silicon dioxide, zirconium oxide, titanium oxide or bismuth oxide; nitrides like aluminium nitride, silicon nitride or sulfides like zinc sulfide have been proposed as the protective layer. As far as the base sheet is considered, it should be transparent, dimensionally stable, chemically uniform and it should have lesser double refraction. Glass is an excellent material that can fulfill these conditions completely. However, in case of glass base sheet there are following defects.

- (1) It is difficult to make reproducible disks on a large scale at low cost.
- (2) Glass is fragile and difficult to handle.

Thus, it is difficult to say that glass is versatile. Resins that are cheaper and reproducible on a large scale are used as the base material. Especially, a resin with methyl methacrylate as the main component (hereafter called as PMMA) and aromatic polycarbonate resin (hereafter called as PC) are used practically.

Problems to be solved by the invention

However, in case of resin substrate for photomagnetic disk, there is a problem of adhesion of substrate and protective layer interface, in addition to the above problems. As stated above, in case of photomagnetic disk, it is common to form a protective layer for magnetic layer protection and enhancement, when the environmental temperature and humidity is changed, the protective layer easily detaches at the interface or cracking occurs due to the difference in contraction and lack of contact and thus it is not of practical usage.

Although, PMMA excels from the viewpoint of double refraction, it absorbs moisture to a large extent and thus it is not dimensionally stable. Further, since, the adhesion between substrate and protective layer interface is bad, the recorded layer may get detached, or cracks may develop in humid atmosphere. On the other hand, although PC is relatively better as far as dimensional stability is concerned. However, when it is used in various types of environments, the recorded layer may get detached or cracks may develop as in

case of PMMA. Moreover, the basic problem originated from its chemical structure is that its double refraction cannot be sufficiently reduced. Thus, various studies have been carried out on resin material for base sheet of photomagnetic disk but satisfactory material could not be obtained, and one can say that this lack of resistance to the environment has caused delay in practical application of photomagnetic disk.

In this regard various attempts like improvement of surface of PMMA and PC or formation of intermediate layer have been made, but they cannot be said to be satisfactory.

The present inventors conducted intensive research on a resin for base sheet for photomagnetic disk having excellent balance of heat resistance and mechanical strength and excellent dimensional stability, and observed that a resin with a portion mainly consisting of aromatic vinyl monomer and polyphenylene ether satisfies the requirements and it was proposed in patent JP60 - 275593.

Further, the present inventors thought that the factors for occurrence of detachment and cracks in case of the photomagnetic disk lie in the resin material itself, which is used as a base sheet. The present inventors intensively studied the adhesion between various resin materials and protective layers and their detachment. As a result it was observed that when a resin with a polymeric portion mainly consisting of aromatic vinyl monomer and polyphenylene ether is used as a resin material for photomagnetic disk, not only the double refraction is reduced, but the detachment and cracking problem is also solved and this led to the present invention. Thus, the objective of this invention is to provide a photomagnetic disk with low double refraction and high resistance to the environment.

Steps to solve the problem

This invention is regarding a photomagnetic disk having a photomagnetic recording medium layer and protective layer on the base sheet wherein a resin comprising a polymeric portion mainly consisting of aromatic vinyl monomer and polyphenylene ether portion is used as a material for base sheet.

A study by the present inventors on application of the photomagnetic disk revealed that there is an excellent adhesion between the above mentioned base sheet resin and protective layer. Thus the above mentioned excellent properties together make the resin of this invention excellent environment resistant material.

Details of this invention are given below.

The base sheet resin material for photomagnetic disk of this invention is a resin consisting of a polymeric portion mainly containing aromatic vinyl monomer and polyphenylene ether portion. Specifically, it is a mixture comprising a polymer portion mainly consisting of aromatic vinyl monomer and polyphenylene ether, their block copolymer or graft copolymer, or their mixture.

The polymeric portion with vinyl monomer as its main component used in this invention is a copolymer containing at least 50% by weight of homopolymer of aromatic vinyl monomer alone and aromatic vinyl monomer. Examples of aromatic vinyl monomer are styrene, α - methyl styrene, m - methyl styrene, p - methyl styrene, o - chloro styrene, m - chlorostyrene, p - chlorostyrene, m - bromostyrene and p - bromostyrene, but styrene is preferred.

Examples of monomers copolymerizing with aromatic vinyl monomers are unsaturated nitriles like acrylonitrile, methacrylonitrile; alkyl esters of methacrylic acid such as methyl methacrylate, n - propyl methacrylate, iso - propyl methacrylate, n - butyl methacrylate, cyclohexyl methacrylate; alkyl esters of acrylic acid such as methyl acrylate, ethyl acrylate, propyl acrylate and butyl acrylate. More examples are methacrylic acid, acrylic acid, maleic anhydride, citraconic acid anhydride, N - methylmaleimide and N - phenylmaleimide.

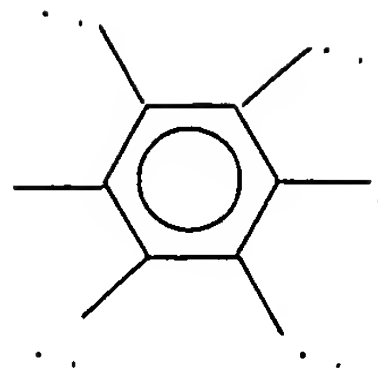
These copolymerizing monomers can be used alone or in the form of mixture, but it is better to adjust the combination and proportion in such a range that transparency of the resin material obtained from copolymer with aromatic vinyl monomer and polyphenylene ether is not affected.

It is preferred that the proportion of aromatic vinyl monomer in the mixture is at least 50% by weight. If it is less than 50% by weight, the obtained resin absorbs moisture to a large extent and is undesirable. It is desirable that the melt flow rate (MFR) of the polymer mainly consisting of aromatic vinyl monomer at 230 °C and 3.8 kg load is 0.5 – 200, preferably in the range of 2 - 100. If it exceeds 200, the mechanical strength reduces and it is undesirable. If, however, it is less than 0.5, it becomes difficult to reduce the double refraction.

The polymer mainly consisting of aromatic vinyl monomer is produced by any of the known methods such as bulk polymerization, emulsion polymerization, solution polymerization using radical initiator, but bulk polymerization is better from the point of productivity and getting a polymer without contamination.

Peroxides like lauryl peroxide, di - tertiarybutyl peroxide, di - cumylperoxide or azo compounds like 2, 2 - azobis isobutyronitrile, 1,1 - azobis (1 - cyclohexanecarbonitrile) can be used as radical initiators. For adjusting the molecular weight, chain transfer agents like tert - butyl, n - butyl, n - octyl, n - dodecyl and tert - dodecyl mercaptan may be added, if necessary. Polymerization is carried out, usually in the temperature range of 50 - 150 °C.

Polyphenylene ether mentioned in this invention is a polymer with repeated monomer units expressed by the general formula



(where, R₁, R₂, R₃ and R₄ are hydrogen, halogen or hydrocarbon group).

The polyphenylene ether is a polymer obtained by oxidative coupling of phenolic monomers and it can be obtained easily by a known method using copper or manganese catalyst (for example JP86 - 18692 and 47 - 86518).

Specific examples of polyphenylene ether are poly (2, 6 - dimethyl - 1, 4 - phenylene) ether, poly (2 - methyl - 6 - ethyl - 1, 4 - phenylene) ether, poly (2 - methyl - 6 - propyl - 1, 4 - phenylene) ether, poly (2, 6 - dipropyl - 1, 4 - phenylene) ether and poly (2 - methyl - bromo - 1, 4 - phenylene) ether, but poly (2, 6 - dimethyl - 1, 4 - phenylene) ether is preferred.

The preferred value of average molecular weight of polyphenylene ether in terms of limiting viscosity (measured in chloroform, at 25 °C) is 0.1 - 1.0. More desirable value is 0.3 - 0.7, and especially desirable value is 0.3 - 0.4. If it is less than 0.1, the double refraction cannot be sufficiently reduced and mechanical strength is also affected. Moreover, if the value is greater than 1.0, uniformity of the resin reduces and fusion fluidity reduces.

In this invention, fused mixing or solution mixing method is used for obtaining the resin for base sheet, by mixing a polymer mainly containing aromatic vinyl monomer with polyphenylene ether.

Fused mixing is carried out in the absence of any solvent, under high shear, at a temperature atleast the glass transition temperature of polyphenylene ether using mixing devices like Banbury mixer, kneader or heat roll. The degree of mixing should be such that both the polymers are dispersed to less than about 1μ, further, it is preferred to mix till molecular scale. Whether the mixing has reached molecular scale can be decided easily by knowing unique glass transition temperature of the mixture. For satisfactory mixing, methods like increasing the mixing temperature, extending the mixing time or increasing the shear are adopted. Further, in fused mixing an organic solvent can be used as plasticizer for making a good mixture, by reducing the glass transition temperature of both the polymers. Organic solvents used in the solution mixing method mentioned above can be used as the organic solvents here. After the completion of mixing, an organic solvent may be evaporated.

In solution mixing method, both the polymers are dissolved in a solvent to make at least 1 weight % solution and made homogeneous by stirring, followed by removal of organic solvent by evaporation. Alternatively, a poor solvent is added to the mixture of the two

polymers to precipitate both the polymers. For this, chloroform, methylene chloride, ethylene chloride, toluene, benzene or chlorobenzene can be used as better organic solvents. Further, methanol, ethanol, propyl alcohol, n - hexane, n - pentane can be used as the poor solvents.

The graft copolymer made from polymer portion mainly containing aromatic vinyl monomer and polyphenylene ether portion can be obtained by polymerizing one of them in the presence of other polymer.

Specifically, aromatic vinyl monomer may be polymerized in the presence of polyphenylene ether as mentioned in JP 42 - 22069, JP40 - 1210, JP 47 - 47862 and JP 52 - 38596. Alternatively, a phenol monomer may be polymerized in the presence of a polymer mainly consisting aromatic vinyl monomer by oxidative coupling, to get graft copolymer or block copolymer.

The proportion of the polymer mainly containing aromatic vinyl monomer and polyphenylene ether portion is such that the former is 20 - 95 weight % and preferably 40 - 75 weight % and that of the latter is 5 - 50 weight % and preferably 25 - 60 weight %.

As the proportion of polyphenylene ether portion is reduced, reduction in double refraction becomes difficult. On the other hand, if the polyphenylene ether portion is too much, the transparency to light rays reduces, melt viscosity of the mixture increases and injection molding becomes difficult.

Double refraction of the molded product obtained according to the molding conditions like resin temperature, molding pressure, die temperature can be adjusted to suit the desired performance of the molded product.

Further, the base material mentioned above can pass semi conducting laser light. Especially, preferable value of transparency for light rays of wavelength 800 nm at thickness 1.2 mm is more than 75 %.

Examples of the methods of molding for obtaining photomagnetic disk of this invention are injection molding, compression molding and injection compression molding. Out of these, injection molding is the most suitable method from the point of productivity.

There is no specific restriction on the photomagnetic disk of this invention and a combination of ordinarily used rare earth elements as the recording medium (like Gd, Tb and Ho) and transition metals (like Fe, Co) can be adopted. This can be obtained by usual methods of making thin alloy films such as vapor deposition or sputtering. Examples of the combination are two elements like TbFe, GdCo, three elements like GdTbFe, TbFeCo or four elements like GdTbFeCo.

Examples of protective layer that can be used in this invention are oxides like aluminium oxide, zirconium oxide, chromium oxide, bismuth oxide or silicon oxide; nitrides like silicon nitride or aluminium nitride; sulfides like zinc sulfide or cadmium sulfide or,

carbides like silicon carbide. When any of these is used, the performance of the resin sheet used in this invention (as regards detachment or occurrence cracks) is improved as compared to PC or PMMA. However, which of them is to be used is decided from the point of the basic objective of prevention of oxidation by the protective layer. More specifically silicon oxide, silicon nitride or zinc sulfide is preferable. This protective layer can be generated by selecting appropriate method from various techniques of thin layer generation such as vapor deposition method, sputtering, reactive sputtering or plasma method. There is no specific restriction on the thickness of the photomagnetic layer or protective layer. But usually it is in the range of 10 - 200 nm.

Result of the invention

This invention is based on the point that it is possible to provide a photomagnetic disk wherein the adhesion between protective layer and base layer is excellent, dimensional stability of the base material and resistance to the environment is high. Thus, this invention is effective in greatly reducing the cost of photomagnetic disk, and making it versatile.

Embodiments

This invention is explained by giving specific examples.

Embodiment 1

Using the method mentioned in No. 9 of working example of JP47 - 86518, 2,6 - xylenol was polymerized by using manganese chloride and ethanol amine as the catalysts to get poly (2, 6 - dimethyl - 1,4 - phenylene) ether of limiting viscosity 0.40 (in chloroform, 25°C).

This polyphenylene ether resin and polystyrene resin (4-62A, MFR 24, Esbrite[®], Manufactured by Nippon polystyrene Industries Ltd.) were mixed in 50:50 proportions. After kneading by an extruder followed by pelletization, a grooved base sheet having dimensions of diameter 130 mm and thickness 1.2 mm (groove pitch was 1.6 μ) was obtained by injection molding at cylinder temperature of 320 °C, die temperature 85 °C.

Silicon reactive sputtering was carried out on this base sheet in the atmosphere of mixture of argon and nitrogen gas under reduced pressure of 5×10^{-2} Torr to get a silicon nitride film of double refraction 2.0 and film thickness 850 Å. Further, a 900 Å magnetic layer of TbFeCo was formed on it by sputtering by the usual method and then 850 Å of above mentioned silicon nitride was formed to get a photomagnetic disk possessing structure of base sheet/ silicon nitride /TbFeCo / silicon nitride.

For comparison, photomagnetic disks were prepared from PMMA (Sumipecks[®] B - MHO, manufactured by Sumitomo Chemicals) and PC (Panlite[®] AD - 5503) by injection molding, as in embodiment 1.

Detachment test was carried out on these disks by using tape. This test was carried out by making a scratch of 1.25 square mm on the disk by means of a knife, sticking Scotch tape #810 (manufactured by Sumitomo 3M Co.) on it, detaching it by hand and measuring the number of mesh detached. The results are presented in Table 1. This has revealed that the photomagnetic disk of this invention adheres more firmly than PC or PMMA.

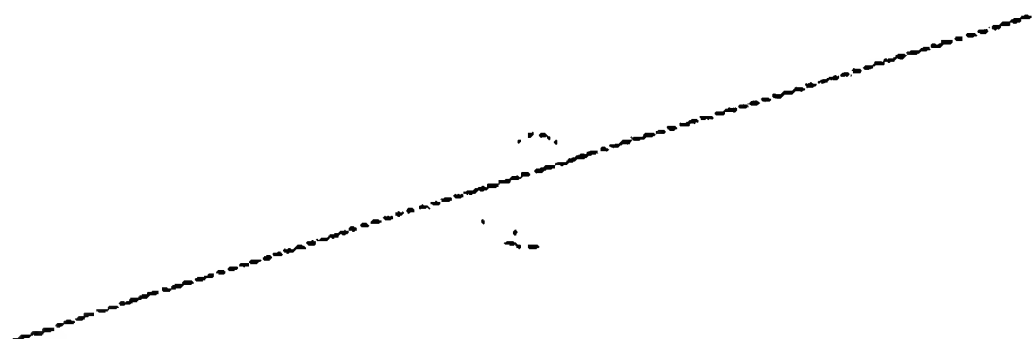


Table 1 Detachment test for photomagnetic disk

Base sheet	Extent of detachment *Note
This invention	1.5
PMMA	97.0
PC	72.0

*Note: Extent of detachment: (No. of mesh detached/ total number of mesh)

By using photomagnetic disk obtained in the same manner, environmental resistance test was carried out by in a thermo - hygostat under the conditions shown in Fig. 1 by using a heat cycle and the change in performance before and after was studied. Performance measurements were made by using photomagnetic disk evaluation device OMS - 1000, manufactured by Nakamichi Co. The results are shown in Table 2. In PMMA and PC, cracks developed in environmental resistance test and performance measurement was not possible, whereas the photomagnetic disk of this invention showed excellent environmental resistance.

Table 2 Environmental resistance test for photomagnetic disk

	Performance before environmental resistance test * 1 (C / N)	Performance after environmental resistance test *1 (C / N)	
		Stored under 60 °C, 80 % RH	Heat cycle test * 2
This invention	46 dB	After 20 days 46 dB (no change in shape)	After 10 days 45 dB (no change in shape)
PMMA	48 dB	Cracks developed while taking out	Cracks developed after 1 day
PC	40 dB	Cracks developed while taking out	Cracks developed after 2 days

*1 Conditions for evaluation: Rotation Speed of disk 1800 rpm

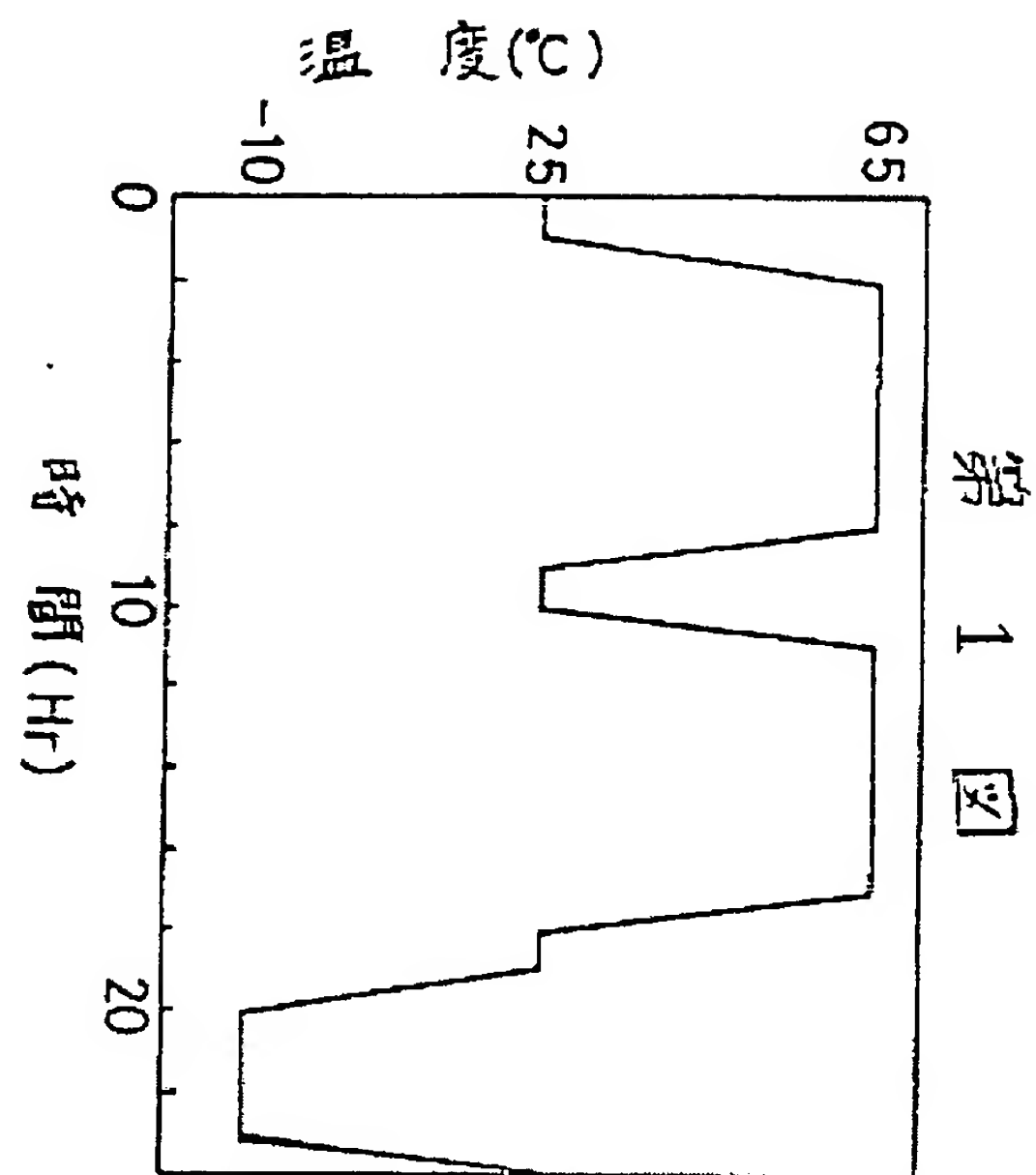
Writing frequency 1MHz duty 50 %

Writing position $r = 30$ mm

*2. Heat cycle conditions

Temperature: 93 ± 3 % RH constant

Temperature: repetition of heat cycle of Fig. 1



4. Brief explanation of the figure

Fig. 1 shows the relation between temperature (in $^{\circ}\text{C}$, vertical axis) and time (in hr, horizontal axis) during environmental test (heat cycle).
